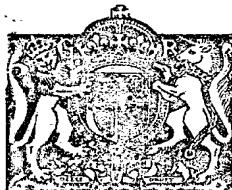


PATENT SPECIFICATION



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COMPLETE SPECIFICATION.

Manufacture of Aromatic Tetrahydronaphthylamines or Derivatives thereof.

I, OLIVER YOUNG IMRAY, a British subject, of 30, Southampton Buildings, London, W.C. 2, do hereby declare the nature of this invention (as communicated to me from abroad by Society of Chemical Industry in Basle, of Basle, Switzerland, a Swiss company), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

According to this invention aromatic tetrahydronaphthylamine derivatives are made in a smooth manner with individual products by subjecting N-substitution products of a naphthylamine to catalytic hydrogenation. When the derivative is an N-acyl-naphthylamine the corresponding tetrahydronaphthylamine may be made by saponifying the product of the hydrogenation.

The process is essentially better than that of Schroeder, namely the nitration of the tetrahydronaphthalene, followed by reduction and separation of the isomerides produced (compare Annalen 426 page 53) in that individual products are obtained directly. Furthermore, it is a considerable simplification of the process using sodium and alcohol and in contrast with these processes produces almost exclusively the aromatic amino-compounds.

The following examples illustrate the invention, the parts being by weight:—

EXAMPLE 1.

85.6 parts of N-ethyl- α -naphthylamine are dissolved in 285 parts of ethyl alcohol and the solution is treated with hydrogen under pressure after addition of 15 parts of nickel catalyst. At about 130° C. and under 30 atmospheres pressure hydrogen is absorbed corresponding with 4 atoms of hydrogen per molecule

of amine. From the product thus made the ar. N-ethyl-tetrahydronaphthylamine is separated by fractional distillation or by converting it into its hydrochloride which is sparingly soluble in hydrochloric acid. The compound boils at 139—142° C. under $8\frac{1}{2}$ mm. pressure.

In like manner ar. 2-N-ethyl-amino-tetrahydronaphthalene may be made from N-ethyl- β -naphthylamine.

EXAMPLE 2.

185 parts of acetyl- α -naphthylamine are made into a paste with 370 parts of alcohol and 15 parts of nickel catalyst are added. This mixture is heated and stirred in hydrogen under 20 atmospheres pressure at 110—120° C., fresh gas being substituted for the hydrogen absorbed. The absorption of hydrogen is free and uniform, and ceases when the proportion corresponding with the formation of the tetrahydro-compound has been taken up. The contents of the autoclave are diluted with alcohol and filtered while hot from the catalyst. From the filtrate the greater part of the ar. 1-acetaminotetrahydronaphthalene crystallises directly in the form of fine needles which melt at 159—160° C. Further quantities may be recovered from the mother liquor by concentration of the latter.

By boiling the compound with sulphuric acid of 70 per cent. strength the acetyl-group may be eliminated.

EXAMPLE 3.

110 parts of acetyl- β -naphthylamine are dissolved in 450 parts of tetrahydronaphthalene and after addition of 15 parts of catalyst the solution is hydrogenised at 130—140° C. as described in Example 1. When the proportion of hydrogen corresponding with the tetrahydro-derivative has been absorbed the

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reaction ceases. The solution, freed from the catalyst, is evaporated in a vacuum and the solidified residue re-crystallised from toluene. The ar. acetyl tetrahydro- β -naphthalide thus obtained melts at 109° C.

By boiling the compound with sulphuric acid of 70% strength it is saponified. The isolated base melts at 38° C. 10 and is identical with the ar. 2-amino-tetrahydronaphthalene described by Schroeder.

EXAMPLE 4.

1 part of acetylated N-ethyl- α -naphthylamine is hydrogenised in 2.5 parts 15 of alcohol in the manner described in Example 1 by hydrogen under 20—30 atmospheres pressure. The product is distilled directly in a vacuum, whereby 20 the acetylated ar. tetrahydro-N-ethyl- α -naphthylamine passes over at 167—168° C. under 8% pressure in the form 25 of an oil as clear as water and soon solidifying. The acetylated ar. tetrahydro-ethyl- α -naphthylamine thus obtained melts at 58° C.

By prolonged boiling with sulphuric acid of 80 per cent. strength the compound is saponified.

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EXAMPLE 5.

87.6 parts of N-phenyl- α -naphthylamine are dissolved in 235 parts of 35 alcohol and the solution is treated after addition of 15 parts of nickel catalyst, with hydrogen under 20—25 atmospheres pressure. Between 80 and 100° C. there is absorption of hydrogen which is interrupted after somewhat more than 4 atoms

of hydrogen per molecule of amine have been taken up. The ar. N-phenyltetrahydro- α -naphthylamine is isolated by distillation in a vacuum. It boils under 8% pressure at 198° C. When freshly distilled it forms a thick oil which solidifies on standing. When recrystallised 45 from petroleum ether it melts at 43.5° C.

The products of this invention are valuable intermediate compounds in the dyestuff industry.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A manufacture of aromatic tetrahydronaphthylamine-derivatives by subjecting an N-substitution product of a naphthylamine to catalytic hydrogenation. 55

2. A manufacture of aromatic tetrahydronaphthylamines or derivatives thereof, by subjecting an N-acetyl derivative of a primary or secondary naphthylamine to catalytic hydrogenation, and saponifying the product. 60

3. Aromatic tetrahydronaphthylamines or derivatives thereof which can be made by the manufacture referred to in Claim 1 or Claim 2, whenever so made or made by any process which is the obvious 70 chemical equivalent of such manufacture.

Dated this 23rd day of February, 1927.

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